## Hollow Co<sub>3</sub>O<sub>4</sub> nanospheres modified with RuCl<sub>3</sub> as

## peroxidase mimics for sensitive determination of

## sulfide ions at neutral pH

Daqing Chen, Minghui Li, Wanzhu Wang, Danhua Ge\*, Xiaojun Chen\*



Fig. S1. (A) SEM and (C) TEM images of carbon nanospheres. (B) SEM and (D)

TEM images of Co<sub>3</sub>O<sub>4</sub> HNSs.



Fig. S2. EDX elements mapping of  $Ru^{3+}$ -Co<sub>3</sub>O<sub>4</sub> HNSs.



Fig. S3. (A)  $N_2$  adsorption-desorption isotherms of  $Co_3O_4$ . (B) Corresponding pore

size distributions.



Fig. S4. The high resolution XPS detailed spectra of Ru 3p of Ru<sup>3+</sup>-Co<sub>3</sub>O<sub>4</sub> HNSs.



Fig. S5. UV-vis absorbance spectra of different reaction systems. a:

TMB+H<sub>2</sub>O<sub>2</sub>+Ru<sup>3+</sup>-Co<sub>3</sub>O<sub>4</sub> for 5 min, b: TMB+H<sub>2</sub>O<sub>2</sub>+Ru<sup>3+</sup>-Co<sub>3</sub>O<sub>4</sub> for 5 min then removing Ru<sup>3+</sup>-Co<sub>3</sub>O<sub>4</sub> and adding S<sup>2-</sup>, c: TMB+H<sub>2</sub>O<sub>2</sub>+Ru<sup>3+</sup>-Co<sub>3</sub>O<sub>4</sub> for 5 min then adding S<sup>2-</sup>, d: Ru<sup>3+</sup>-Co<sub>3</sub>O<sub>4</sub>+S<sup>2-</sup> for 5 min then adding TMB+H<sub>2</sub>O<sub>2</sub>.



Fig. S6. (A) Reproducibility and (B) stability of Ru<sup>3+</sup>-Co<sub>3</sub>O<sub>4</sub> HNSs.

					5	
Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
С	Κ	13.16	2.55	4.57	0.57	6.43
0	Κ	42.28	11.47	19.56	4.45	1.94
Cl	Κ	0.8	0.26	0.82	0.24	19.59
Со	Κ	43.38	9.81	73.94	12.62	0.77
Ru	L	0.38	0.11	1.11	0.27	18.55

Table S1. EDX element contents of Ru<sup>3+</sup>-Co<sub>3</sub>O<sub>4</sub>.

**Table S2.** The optimum pH value of S<sup>2-</sup> was detected by different nanozymes.

Catalyst	Optimum pH value	Ref.
CuCo <sub>2</sub> O <sub>4</sub> NWs	4.0	1
ZnS NPs	4.0	2
FePPOP <sub>EPA</sub>	3.39	3
Ag-Fe <sub>3</sub> O <sub>4</sub>	3.5	4
SnTe	4.0	5
GBR	4.48	6
Fe-PPOP	3.6	7
Ru <sup>3+</sup> -Co <sub>3</sub> O <sub>4</sub> HNSs	7	This work

Table S3. Comparison of the apparent Michaelis constant  $(K_m)$ .

Catalyst	K <sub>m</sub> /i	mM	Dof
	TMB	$H_2O_2$	Kel.

HRP	0.43	1.21	8
Mo-CQDs	0.38	0.05	9
Ru NPs	0.234	2.206	10
Pt/CuCo <sub>2</sub> O <sub>4</sub>	0.24	0.41	1
NGZF	0.907	115.52	11
Ru <sup>3+</sup> -Co <sub>3</sub> O <sub>4</sub> HNSs 🗆	0.39	0.25	This work

Table S4. Comparison of different nanozymes for the colorimetric detection of

<u>~</u>.

	$S^{2^{2}}$ 10ns.		
Material	Linear range (µM)	LOD (nM)	Ref.
βFeOOH	5-30	2190	12
Au@Ag	1.5-10	500	13
Pt/CuCo <sub>2</sub> O <sub>4</sub>	0.5-10	85.9	1
Ag	0.8-6.4	350	14
Carrageenan-Silver	2.5-1000	1700	15
SA Fe/B-g-C <sub>3</sub> N <sub>4</sub>	1-10	570	16
GMP-Cu	2-220	670	17
Ru <sup>3+</sup> -Co <sub>3</sub> O <sub>4</sub> HNSs	0.5-20	51	This work

## Reference

- Y. Xue, H. Li, T. Wu, H. Zhao, Y. Gao, X. Zhu and Q. Liu, Pt deposited on sea urchin-like CuCo<sub>2</sub>O<sub>4</sub> nanowires: Preparation, the excellent peroxidase-like activity and the colorimetric detection of sulfide ions, *J. Environ. Chem. Eng.*, 2022, 10, 107228.
- S. Song, D. Song, H. Tang, B. Kang, J. Lv, H. Lu and Z. Zhao, Ionogels as precursors to prepare ZnS nanoparticles for colorimetric sensing of sulfide ions, *ACS Sustain. Chem. Eng.*, 2020, 8, 759-770.
- 3. Y. Li, Y. Fang, W. Gao, X. Guo and X. Zhang, Porphyrin-based porous organic polymer as peroxidase mimics for sulfide-ion colorimetric sensing, *ACS Sustain. Chem. Eng.*, 2020, **8**, 10870-10880.
- Y. Wang, Y. Ding, Y. Tan, X. Liu, L. Fu and W. Qing, Ag-Fe<sub>3</sub>O<sub>4</sub> nanozyme with peroxidase-like activity for colorimetric detection of sulfide ions and dye degradation, *J. Environ. Chem. Eng.*, 2023, 11, 109150.
- 5. Y. Qu, T. Chen and Y. Xu, Selective and smart dual-channel colorimetric sulfur ion sensing readout platform, *Sensor. Actuat. B-Chem.*, 2023, **392**, 134060.
- 6. S. Singh, K. Mitra, A. Shukla, R. Singh, R. K. Gundampati, N. Misra, P. Maiti and

B. Ray, Brominated graphene as mimetic peroxidase for sulfide ion recognition, *Anal. Chem.*, 2017, **89**, 783-791.

- 7. L. Liao, D. Guo, X. Luo, L. Meng and F. Wu, Facile fabrication of iron porphyrinbased porous organic polymer with excellent oxidase-like activity for colorimetric detection of sulfide, *Colloid Surface A*, 2022, **651**, 129727.
- 8. Y. Guo, L. Deng, J. Li, S. Guo, E. Wang and S. Dong, Hemin-graphene hybrid nanosheets with intrinsic peroxidase-like activity for label-free colorimetric detection of single-nucleotide polymorphism, *ACS Nano*, 2011, **5**, 1282-1290.
- L. Zhao, Z. Wu, G. Liu, H. Lu, Y. Gao, F. Liu, C. Wang, J. Cui and G. Lu, Highactivity Mo, S co-doped carbon quantum dot nanozyme-based cascade colorimetric biosensor for sensitive detection of cholesterol, *J. Mater. Chem. B*, 2019, 7, 7042-7051.
- G.-J. Cao, X. Jiang, H. Zhang, T. R. Croley and J.-J. Yin, Mimicking horseradish peroxidase and oxidase using ruthenium nanomaterials, *RSC Adv.*, 2017, 7, 52210-52217.
- D. Navadeepthy, A. Rebekah, C. Viswanathan and N. Ponpandian, N-doped graphene/ZnFe<sub>2</sub>O<sub>4</sub>: A novel nanocomposite for intrinsic peroxidase based sensing of H<sub>2</sub>O<sub>2</sub>, *Mater. Res. Bull.*, 2017, **95**, 1-8.
- 12. R. Purbia and S. Paria, Green synthesis of single-crystalline akaganeite nanorods for peroxidase mimic colorimetric sensing of ultralow-level vitamin B1 and sulfide ions, *ACS Appl. Nano Mater.*, 2018, **1**, 1236-1246.
- W. Liu, Z. Li, H. Jia, L. Zhang, W. He and Q. Meng, Shell surface sulfidation mediated the plasmonic response of Au@Ag NPs for colorimetric sensing of sulfide ions and sulfur, *Appl. Surf. Sci.*, 2019, 481, 678-683.
- 14. K. Shanmugaraj and M. Ilanchelian, Colorimetric determination of sulfide using chitosan-capped silver nanoparticles, *Microchimica Acta*, 2016, **183**, 1721-1728.
- 15. Y. Wang, X. Dong, L. Zhao, Y. Xue, X. Zhao, Q. Li and Y. Xia, Facile and green fabrication of carrageenan-silver nanoparticles for colorimetric determination of Cu<sup>2+</sup> and S<sup>2-</sup>, *Nanomater. -Basel*, 2020, **10**, 83.
- Z. Xiao, K. Qu, F. Ye, J. Zheng, Y. Wang, H. Wang, Q. Xu and J. Xu, B-doped graphite carbon nitride loaded Fe single atoms with enhanced peroxidase-like activity, *Sci. China Mater.*, 2023, 66, 3592-3600.
- H. Huang, M. Li, M. Hao, L. (Lucy) Yu and Y. Li, A novel selective detection method for sulfide in food systems based on the GMP-Cu nanozyme with laccase activity. *Talanta*, 2021, 235, 122775.